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(54) Title of the invention A polyamide resin composition

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## Specification

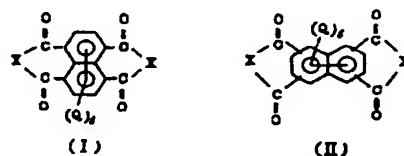
### 1. Title of the Invention

A polyamide resin composition

### 2. Scope of Claims

(1) A polyamide resin composition which is characterized in that it is formed by adding at least 0.001 part by weight of at least one of the group comprising optionally-substituted naphthalenetetracarboxylic acids, optionally-substituted naphthalenedicarboxylic acids, and the anhydrides, imides and esters of these, per 100 parts by weight of a polyamide resin.

(2) A composition according to Claim 1 where the optionally-substituted naphthalenetetracarboxylic acid anhydrides and imides are represented by general formulae (I) and (II) below,



(X represents an oxygen atom or a group  $\text{NR}^1$ , where a plurality of groups  $\text{R}^1$  may be identical or different and in each case  $\text{R}^1$  represents a hydrogen atom, halogen atom, OH, optionally-substituted alkyl, alkenyl, aryl, aralkyl or alkylaralkyl group; Q represents a halogen atom, OH,  $\text{NH}_2$ ,  $\text{NO}_2$ , CN,  $\text{SO}_3\text{H}$  or salt thereof, optionally-substituted alkyl, alkoxy, alkenyl, aryl, aralkyl or alkylaralkyl group; and  $\ell$  is an integer in the range 0 to 4).

(3) A composition according to Claim 1 where the optionally-substituted naphthalenedicarboxylic acids and the anhydrides, imides and esters thereof, are represented by the following general formulae (III) and (IV),



(where X is an oxygen atom or the group  $\text{NR}^4$  and  $\text{R}^4$  has the same meaning as  $\text{R}^1$  in general formulae (I) and (II);  $\text{R}^2$  and  $\text{R}^3$  may be the same or different and they each represent a hydrogen atom, halogen atom, optionally-substituted alkyl, alkenyl, aryl, aralkyl or alkylaralkyl group; Q is the same as Q in general formulae (I) or (II) above; and m is an integer in the range 0 to 6; and, furthermore, the anhydride group or imide group in (IV) is formed at the 1,8-, 2,3- or 1,2-positions on the naphthalene ring).

### 3. Detailed Description of the Invention

#### [Industrial Field of Application]

The present invention relates to a polyamide resin composition. More specifically, it relates to a polyamide resin composition which is outstanding in its ultraviolet light screening property.

#### [Prior-Art]

Nylon 6 and other polyamides are outstanding in their mechanical properties including flexibility, and in their chemical properties such as chemical resistance,

etc, and so are used for various types of film including food packaging.

Furthermore, non-crystalline polyamides are employed for various kinds of container on account of their transparency, as well as their chemical resistance and mechanical properties.

However, while these polyamide films and containers are extremely outstanding in their ultraviolet light screening properties on the short wavelength side up to about 300 nm, they are essentially transparent to ultraviolet light on the long wavelength side above this and to visible light. This is a cause of the deterioration of the contents when stored for a prolonged period and, generally speaking, efforts have been made to overcome this disadvantage by adding ultraviolet light absorbers.

However, these ultraviolet light absorbers are usually expensive and, furthermore, their application process is complex. In addition, such compounds generally tend to exhibit sublimation and their thermal stability is usually poor, so that troubles can often arise during the application process or at the time of mould processing. Moreover, when used in containers or in packaging for foods, there is a fear of them migrating to the contents.

#### [Objective of the Invention]

As a result of a painstaking investigation into ultraviolet light absorbers which meet the desired objectives, the present inventors have discovered a

polyamide resin composition which does not just show screening properties on the short wavelength side but can also adequately screen ultraviolet on the long wavelength side. It is on this discovery that the present invention is based.

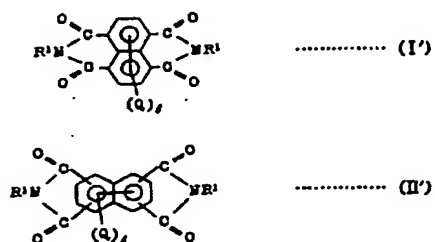
Specifically, the present invention is polyamide resin composition which is characterized in that it is formed by adding at least 0.001 part by weight of at least one of the group comprising optionally-substituted naphthalenetetracarboxylic acids, optionally-substituted naphthalenedicarboxylic acids, and the anhydrides, imides and esters of these, per 100 parts by weight of a polyamide resin.

[Constitution of the Invention]

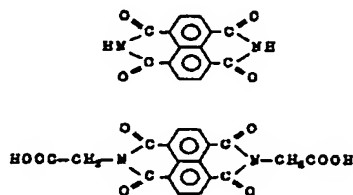
The present invention is now explained in detail.

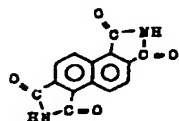
One or more compounds selected from the group comprising optionally-substituted naphthalenetetracarboxylic acids, optionally-substituted naphthalenedicarboxylic acids, and the anhydrides, imides and esters of these, is/are used as the compound(s) added to the polyamide resin in the present invention. As the optionally-substituted naphthalenetetracarboxylic acid diimides, there can be used the diimide compounds represented by the following general formulae (I') and (II'). These can be produced for example by the reaction between the naphthalenetetracarboxylic acid or a naphthalene-tetracarboxylic acid derivative and ammonia, an aliphatic amino-carboxylic acid such as glycine, alanine, valine or  $\epsilon$ -aminocaproic acid, an amino-alcohol, an aromatic amino-carboxylic acid such as o-, m- or p-aminobenzoic acid, or a diamine.

Preferred examples of the diimides are the compounds represented by the following general formulae (I') and (II')



(where, in formulae (I') and (II'), the groups R<sup>1</sup> may be the same or different and each represents a hydrogen atom, halogen atom, hydroxy group or optionally substituted alkyl group, alkenyl group, aryl group, aralkyl group or alkylaralkyl group; Q represents a halogen atom, hydroxy group, amino group, nitro group, cyano group, sulphonic acid group or salt thereof, optionally-substituted alkyl group, alkoxy group, alkenyl group, aryl group, aralkyl group or alkylaralkyl group; and *x* is an integer in the range 0 to 4). The following are specific examples:-





Various types of ester can be used as the aforesaid naphthalene-tetracarboxylic acid esters, such as the methyl, ethyl, propyl, butyl and other alkyl esters.

Examples of the aforesaid optionally-substituted naphthalene-dicarboxylic acids are those shown by general formula (III) below, such as the 2,6-, 2,7-, 2,3-, 1,8-, 1,7-, 1,6-, 1,5-, 1,4-, 1,3- and 1,2-naphthalenedicarboxylic acid structural isomers. These may have one or more ring substituent groups.

Specifically, taking the example of the 2,6-naphthalenedicarboxylic acid, there are the 4-chloro-, 4,5-dichloro-, 4,8-dichloro-, 4-bromo-, 4,5-dibromo-, 4,8-dibromo-, 4-ethoxy-, 4,5-diethoxy-, 4,8-diethoxy-, 4-amino-, 4,5-diamino-, 4-nitro-, 4,5-dinitro-, 4-hydroxy-, 4,5-dihydroxy- and other such derivatives. These naphthalenedicarboxylic acids may also be in the form of the acid anhydrides represented by formula (IV), examples of which are the 1,8-, 2,3- and 1,2-naphthalenedicarboxylic anhydrides, 4-hydroxy-1,8-naphthalenedicarboxylic anhydride and, also, in the same way, the 4-chloro and 4,5-dichloro- derivatives, etc.



(In formula (III),  $R^2$  and  $R^3$  may be the same or different and they each represent a hydrogen atom, halogen atom, optionally-substituted alkyl group, alkenyl group, aryl group, aralkyl group or alkylaralkyl group. In formula (IV), X represents an oxygen atom or the group  $NR^4$ , where  $R^4$  has the same meanings as  $R^1$  above. Furthermore, the acid anhydride group or imide group may



form a ring at positions 1,2, 1,8 or 2,3. Q is the same as that in aforesaid general formulae (I) and (II) and m is an integer in the range 0 to 6.)

Preferred examples of the naphthalenedicarboxylic acid esters are the methyl, ethyl, propyl and butyl esters. Furthermore, as imide compounds, there may be used any naphthalenedicarboxylic acid imide represented by general formula (IV). Specific examples are 1,8-naphthalenedicarboxylic acid imide, 1,8-naphthalenedicarboxylic acid-N-( $\alpha$ -carboxymethyl)imide and the corresponding -( $\beta$ -carboxyethyl)imide, -(o- (m- or p-)carboxyphenyl)imide, -( $\alpha$ -bromomethyl)imide, -( $\alpha$ -hydroxymethyl)imide and the like.

These naphthalenedicarboxylic acid imides can be produced for example by the reaction between the naphthalenedicarboxylic acid or naphthalenedicarboxylic acid derivative and ammonia, an aliphatic amino-carboxylic acid such as glycine, alanine, valine, leucine or  $\epsilon$ -aminocaproic acid, an amino-alcohol such as ethanolamine, an aromatic amino-carboxylic acid such as o-, m- or p-aminobenzoic acid, or a diamine such as hexamethylenediamine.

The amount of the naphthalenetetracarboxylic acid, naphthalenedicarboxylic acid or derivative of these added will be at least 0.001 part by weight per 100 parts by weight of the polyamide resin. If there is less than 0.001 part by weight, then a sufficient ultraviolet light screening effect is not obtained. It is particularly preferred that the added amount be in the range 0.005 to 10 parts by weight.

In the present invention, in order that the ultraviolet light screening effect is more effectively exhibited, it is preferred that there be jointly used a naphthalene-tetracarboxylic acid or derivative thereof and a naphthalenedicarboxylic acid or derivative thereof. When jointly used in this way, the preferred amount added is from 0.01 to 10 parts by weight.

The compound with the naphthalenetetracarboxylic acid skeletal structure or the compound with the naphthalenedicarboxylic acid skeletal structure may be added at any stage of the polyamide production or it may also be added at any stage before mould-processing. In whichever case, it is possible to manifest an ultraviolet light screening effect in the same way.

That is to say, addition may be carried out at any stage up to the completion of the polyamide moulding, such as prior to commencement of the polymer synthesis reaction, during the polymer synthesis reaction, following the completion of the polymer synthesis reaction, in the powder state or in the moulding stage.

The polyamide resin in the present invention may be any such polymer providing it is thermoplastic and has amide bonds in the main chain of the polymer.

Typical examples are nylon-4, nylon-6, nylon-12, nylon-6,6, nylon-6,10, nylon comprising m-xylylenediamine and adipic acid, nylon comprising hexamethylenediamine and isophthalic acid and/or terephthalic acid, nylon comprising trimethylhexamethylenediamine and terephthalic acid, and nylon formed by the copolymerization of 12-lactam and bis(4-amino-3-methyl-

cyclohexyl)methane and isophthalic acid. However, of course, there is no restriction to these particular examples. Furthermore, there may also be employed blends of the aforesaid thermoplastic polyamide resins or blends of these thermoplastic polyamide resins and other thermoplastic resins such as polyesters, polycarbonates, polyethylene-vinyl alcohol copolymer and the like.

Again, there is no objection to adding conventional additives such as stabilizers, mould release agents, antistatic agents, dispersants and colouring agents, etc, to the polyamide resin composition of the present invention.

The polyamide resin composition with outstanding ultraviolet light screening properties obtained in the present invention may be melted and moulded to form moulded articles. In such circumstances, all the methods normally used for the moulding of polyamides can be employed. Specifically, there may be used ordinary extrusion moulding, injection moulding, extrusion blow moulding and injection blow moulding methods, to form film, injection moulded pieces and bottles. Furthermore, these primary moulded articles may themselves be subjected to secondary processing such as uniaxial or biaxial drawing, lamination, vacuum forming or the like. In addition, at the time of moulding, where required there may be produced a laminate with some other thermoplastic resin such as a polyolefin, polyester, modified polyolefin, ionomer or the like.

[Examples]

Below, the present invention is explained in further detail by means of examples. The various property values were measured under the following conditions.

- Relative viscosity ( $\eta_{rel}$ )

This was measured at a concentration of 0.01 g/cc in 98% concentrated sulphuric acid at 25°C.

- Ultraviolet light transmittance

Measurement was carried out in the normal way using a Hitachi Spectrophotometer model 340.

#### Example 1

11.0 g of acetic acid and 5.0 g of naphthalene-1,4,5,8-tetracarboxylic dianhydride were added to an aqueous nylon salt solution comprising

90% aq. solution of hexamethylenediamine	2.28 kg
water	9.0 kg
isophthalic acid	1.96 kg
terephthalic acid	0.98 kg

and the mixture introduced into a reactor equipped with a stirrer. After thoroughly purging with nitrogen, heating and raising of pressure were carried out until the pressure within the system was 18 kg/cm<sup>2</sup>. Having reached 18 kg/cm<sup>2</sup>, stirring was carried out while releasing the pressure so that the internal pressure remained at 18 kg/cm<sup>2</sup>, and the polymerization reaction commenced. During this period, the internal temperature rose slowly from 210°C and after 5 hours there was practically no further distillation of water. At this

point the internal temperature was 250°C. The pressure was then further released, and after lowering the pressure until the pressure in the system finally reached 700 mmHg, the pressure was returned to normal. Molten polymer was removed from the bottom of the reactor.

This polymer comprised a polyamide resin in which there was 100 wt% of polyamide component derived from an aliphatic diamine plus isophthalic and terephthalic acids. Its relative viscosity  $\eta_{rel}$  was 2.1.

The polyamide was vacuum-dried in the normal way, after which it was moulded in the form of sheet of thickness 350  $\mu$ m using a 30 mm diameter extruder set at a cylinder and nozzle region temperature of 280°C, a screw rotation rate of 40 rpm and an extrusion rate of 80 g/min.

The light transmittance of this sheet at 370 nm was 2.8%.

#### Example 2

11.0 g of acetic acid and 5.0 g of naphthalene-1,4,5,8-tetracarboxylic dianhydride were added to an aqueous nylon salt solution comprising

90% aq. solution of hexamethylenediamine	2.28 kg
water	9.0 kg
isophthalic acid	1.96 kg
terephthalic acid	0.98 kg
caprolactam	0.77 kg

and the mixture introduced into a reactor equipped with a stirrer. After thoroughly purging with nitrogen, heating and raising of pressure were carried out until

the pressure within the system was 18 kg/cm<sup>2</sup>. Having reached 18 kg/cm<sup>2</sup>, stirring was carried out while releasing the pressure so that the internal pressure remained at 18 kg/cm<sup>2</sup>, and the polymerization reaction commenced. During this period, the internal pressure rose slowly from 210°C and after 5 hours there was practically no further distillation of water. At this point the internal temperature was 250°C. The pressure was then further released, and after lowering the pressure until the pressure in the system finally reached 700 mmHg, the pressure was returned to normal. Molten polymer was removed from the bottom of the reactor.

This polymer comprised a polyamide resin in which there was 85 wt% of polyamide component derived from aliphatic diamine plus isophthalic and terephthalic acids, and 15 wt% of polyamide component derived from the lactam. Its relative viscosity  $\eta_{rel}$  was 2.0.

Sheet of thickness 350  $\mu$ m was obtained by moulding this polyamide resin in the same way as in Example 1.

The light transmittance of the sheet at 370 nm was 1.5%.

### Example 3

An aqueous diamine solution comprising

74 wt% hexamethylenediamine aqueous solution	158.5 g
bis(3-methyl-4-aminocyclohexyl)methane	13.1 g
distilled water	170.0 g

was heated to 70°C, after which 118.0 g of isophthalic acid and 59.0 g of terephthalic acid were added and a uniform nylon salt solution obtained. This was introduced into an autoclave. Furthermore, 1.00 g of acetic acid plus 0.5 g of naphthalene-1,4,5,8-tetracarboxylic dianhydride were added, after which heating was commenced. When the pressure reached 2.5 kg/cm<sup>2</sup>, the autoclave valve was opened and concentration commenced by distilling off water while maintaining the pressure at 2.5 kg/cm<sup>2</sup>. During the concentration, the temperature rise continued and, when the internal temperature reached 190°C, the autoclave valve was closed, following which the increase in temperature continued. When the pressure reached 14 kg/cm<sup>2</sup>, the autoclave valve was again opened and concentration carried out by distilling off water while maintaining the pressure at 14 kg/cm<sup>2</sup>. During this period, the temperature rise continued and, when the internal temperature reached 260°C, pressure release was carried out. After returning the pressure to atmospheric, reaction was continued for 1 hour. Following the end of the reaction, the polymer obtained was discharged from the autoclave under nitrogen and formed into pellets.

The polyamide resin was pressed at 260°C and a 350 μm pressed sheet obtained.

The light transmittance of the sheet at 370 nm was 1.0%.

#### Example 4

Production was carried out in the same way as in Example 1 except that, instead of the naphthalene-1,4,5,8-

tetracarboxylic dianhydride in Example 1, there was added 4 g of 1,4,5,8-naphthalenetetracarboxylic acid-di( $\alpha$ -carboxymethyl)diimide and 20 g of naphthalene-2,6-dicarboxylic acid. A polyamide resin of  $\eta_{rel}$  2.1 was obtained.

The light transmittance at 380 nm of a sheet of thickness 350  $\mu$  obtained by moulding this polyamide resin in the same way as in Example 1 was 0.1%.

#### Comparative Example 1

Polyamide resin of  $\eta_{rel} = 2.1$  was obtained in exactly the same way as in Example 1 except that there was no addition of the naphthalene-1,4,5,8-tetracarboxylic dianhydride.

The ultraviolet light transmittance of 350  $\mu$  sheet obtained by moulding this polyamide resin in the same way as in Example 1 was 77% at 370 nm and 79% at 380 nm.

#### Example 5

0.15 part of naphthalene-1,4,5,8-tetracarboxylic acid di-( $\alpha$ -carboxymethyl)diimide was added to 100 parts by weight of a polyamide resin obtained by the same procedure as in Comparative Example 1, and then thorough mixing carried out in a V-blender, after which a 350  $\mu$  transparent sheet was moulded in the same way as in Example 1.

The light transmittance at 380 nm of this sheet was 0.1%.



#### Example 6

A sheet was moulded in the same way as in Example 1 except that instead of using naphthalene-1,4,5,8-tetracarboxylic dianhydride there was employed 22 g of 2,6-naphthalenedicarboxylic acid. The light transmittance of this sheet at 370 nm was 2.9%.

#### Example 7

A sheet was moulded in the same way as in Example 2 using 22 g of 2,6-naphthalenedicarboxylic acid instead of the naphthalene-1,4,5,8-tetracarboxylic dianhydride. The light transmittance of this sheet at 370 nm was 1.5%.

#### Example 8

Pellet formation was carried out in the same way as in Example 3 using 1.35 g of 2,6-naphthalenedicarboxylic acid instead of the naphthalene-1,4,5,8-tetracarboxylic dianhydride. This polyamide resin was moulded by the same method as in Example 1 and sheet of thickness 350  $\mu$  obtained. The light transmittance of this sheet at 370 nm was 1.2%.

#### Example 9

0.15 part of 2,3-naphthalenedicarboxylic acid-N-( $\alpha$ -carboxymethyl)imide was added to 100 parts by weight of a polyamide resin obtained by the same procedure as in Comparative Example 1, and then thorough mixing carried out in a V-blender, after which vacuum drying was performed and a 350  $\mu$  transparent sheet moulded in the same way as in Example 1.

The light transmittance of this sheet at 380 nm was 0.1%.

[Effects of the Invention]

As explained above, the polyamide resin composition of the present invention has outstanding ultraviolet screening properties and, in particular, is outstanding in its screening properties on the long wavelength side, when moulded as film or as a container.

**4. Brief Explanation of the Drawing**

Figure 1 is a chart showing the ultraviolet light transmittance as a function of wavelength in the case of sheet moulded using the composition from Example 1 and from Comparative Example 1.

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Figure 1

